

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 227 037 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: 24.07.91 (51) Int. Cl.⁵: **C08J 5/18**, **C08L 23/02**,
C08K 3/00
- (21) Application number: 86117615.4
- (22) Date of filing: 17.12.86

(54) Process for producing a porous film.

(30) Priority: 23.12.85 JP 287909/85

(43) Date of publication of application:
01.07.87 Bulletin 87/27

(45) Publication of the grant of the patent:
24.07.91 Bulletin 91/30

(84) Designated Contracting States:
CH DE FR GB IT LI NL SE

(56) References cited:
EP-A- 0 066 672
FR-A- 2 505 251
GB-A- 2 027 637
GB-A- 2 151 538

(73) Proprietor: **MITSUI TOATSU CHEMICALS INC.**
No. 2-5, Kasumigaseki 3-chome
Chiyoda-Ku Tokyo 100(JP)

(72) Inventor: **Tsuji, Syoichi**
5 Takihar-cho Minami-ku
Nagoya-shi Aichi(JP)
Inventor: **Ito, Michiyasu**
68 Hoshikawa
Kuwana-shi Mie(JP)
Inventor: **Matsumura, Shuji**
55 Narumi Mitakane Midori-ku
Nagoya-shi Aichi(JP)
Inventor: **Suzuki, Hisatosi**
16-84 Aza Nagai Onishi-cho
Okazaki-shi Aichi(JP)
Inventor: **Ito, Syoichi**
2-8-3 Soike-cho Minami-ku
Nagoya-shi Aichi(JP)

(74) Representative: **Strehl, Schübel-Hopf, Groen-**
Ing
Maximilianstrasse 54 Postfach 22 14 55
W-8000 München 22(DE)

EP 0 227 037 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

This invention relates to a process for producing a porous film having flexibility and a structure of uniform fine pores and hence superior water vapor permeability and water resistance and is useful for waterproof clothings, waterproof covers and packaging materials.

10

2. Description of the Related Art

There has so far been known a process for producing a porous film by blending non-compatible substances such as inorganic fine powders with a polyolefin resin in a specified proportion, followed by melt-molding the resulting blend into a film or sheet and then uniaxially or biaxially stretching the film or sheet.

However, such a process has had a drawback that since the resin is stretched and oriented by stretch processing, the hardness of the film or sheet increases so that its flexibility is damaged.

In order to overcome such a problem, the following processes for producing a porous film have been proposed:

- (1) a process of blending a thermoplastic elastomer with a polyolefin resin and a filler (Japanese patent application laid-open No. Sho 59-30833/1984);
- (2) a process of blending a liquid or waxy hydrocarbon polymer with a polyolefin resin and a filler (U.S.-A 4,472,328); and
- 25 (3) a process of blending barium sulfate as an inorganic fine powder with a polyolefin resin (GB-A 2,151,538).

However, porous films obtained according to these production processes have the following practical drawbacks:

According to the process (1), the resulting porosity is insufficient and the water vapor permeability is inferior. According to the process (2), the resulting porous film has a problem that in the high temperature atmosphere or after a long time lapse, hydrocarbon polymers bleed out on the surface of the resulting film so that the surface is sticky. According to the process (3), the resulting porous film has a good flexibility and sufficient water vapor permeability, but the stretching stability i.e. the high stretchability is inferior. Further, as a problem in common to these processes, it is impossible to produce an extremely thin film of about 20 μm . Furthermore, another process of blending a third component brings about a large increase in cost.

SUMMARY OF THE INVENTION

40 The object of the present invention is to provide a process for producing a porous film which comprises a polyolefin resin having a superior solvent resistance, which has practically sufficient mechanical strengths and a good flexibility and also has uniform fine pores and high moisture vapor permeability, and further an extremely thin porous film.

The present invention resides in a process for producing a porous film which comprises blending 30 to 80 parts by weight of an inorganic fine powder having a specific surface area of 15 m^2/g or less and an average particle size of 0.4 to 4 μm with 20 to 70 parts by weight of a polyolefin resin, these parts by weight being based on 100 parts by weight of the blend, followed by melt-molding the resulting blend into a film and then stretching the film to 2 to 7 times the original length at least in the uniaxial direction.

60 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Examples of the polyolefin resin used in the present invention are polypropylene, low density polyethylene, linear low density polyethylene, high density polyethylene and mixtures thereof. Among these, linear low density polyethylene and blends containing linear low density polyethylene are particularly preferred. Examples of the comonomer component for linear low density polyethylene are generally butene, 4-methylpentene, hexene, octene, decene and among these, 4-methylpentene and octene are preferred in the aspect of moldability and physical properties of products.

The inorganic fine powder used in the present invention is fine particles having a specific surface area

of 15 m²/g or less and an average particle size of 0.4 to 4 μm. Examples of the inorganic fine powder used in the present invention are calcium carbonate, magnesium carbonate, magnesium oxide, barium sulfate, silica, aluminum hydroxide, alumina. Among these, precipitated calcium carbonate and precipitated barium sulfate are preferred since such materials have a uniform particle diameter and specific surface area and when they are blended with the resin component and the resulting blend is molded, they have superior dispersibility and the blend has superior processability. Further, the inorganic fine powder is preferred to have a spherical shape. Precipitated barium sulfate is usually obtained for example by the reaction of barium sulfide with an aqueous solution of sodium sulfate or the reaction of barium sulfide with sulfuric acid. The shape includes amorphous shape, spindle shape, plate shape, diamond shape and spherical shape. When the concentrations of barium sulfide and SO₄²⁻, the mechanical conditions of the reaction and the reaction temperature are set under specified conditions, precipitated barium sulfate having a desired average particle size is obtained.

Further, the precipitated calcium carbonate is usually formed by introducing carbon dioxide into an aqueous suspension of calcium hydroxide. It has a cubic shape having an average particle size of 1 μm or less or a spindle shape or an acicular shape having an average particle size of 1 μm or more. When the reaction temperature of the aqueous suspension of calcium hydroxide, addition of a particular salt and the termination time of the reaction are set under specified conditions, a spherical precipitated calcium carbonate having a desired average particle size is obtained.

The specific surface area of the inorganic fine powder is 15 m²/g or less and a range of 0.5 to 5 m²/g is preferred. If the specific surface area exceeds 15 m²/g, the shape of the inorganic fine powder becomes amorphous shape, plate shape or acicular shape so that the particle size distribution becomes broad and the stretchability of film becomes lowered; hence no good porosity is obtained. Further, the porosity of the surface of the fine powder increases and due to the volatile components such as moisture attached to the pores, foaming is observed at the time of melt-molding, the pore size of the resulting film is increased and its water-resistance is remarkably reduced.

The average particle size of the inorganic fine powder is preferably in the range of 0.4 to 4 μm, more preferably in the range of 0.6 to 2 μm. If the average particle size exceeds 4 μm, the stretchability of the film is inferior and stretching breakage occurs prior to uniform stritening. Thus, the production stability is inferior to make uniform pore-formation impossible.

On the other hand, if the average particle size is less than 0.4 μm, the mineral fine powder cannot be highly filled to be unable to make the resulting film porous.

In the resin composition of the present invention, the quantity of the inorganic fine powder is in the range of 30 to 80 parts by weight, preferably 30 to 70 parts by weight based on 100 parts by weight of the blend. With the quantity of less than 30 parts by weight, no good porosity can be obtained in respect of the stretched film. If the quantity exceeds 80 parts by weight, kneadability, dispersibility and stretchability are inferior; thus naturally the water vapor permeability is also inferior and the flexibility lowers.

Next, the process for producing the porous film of the present invention will be described. First, an inorganic fine powder is mixed with a polyolefin resin in specified proportions. The mixing process has no particular limitation. In general, the materials are mixed by means of a blender, followed by blending the mixture by means of a Banbury mixer or another melt-kneader in advance, thereafter pelletizing the blend or not pelletizing it and then sheeting by means of a conventional sheet-molding machine. It is possible to optionally add various additives such as lubricant e.g. calcium stearate, pigment, stabilizers such as those against heat, light and others, plasticizer, antistatic agent.

The film is generally made by calendering, casting or extrusion, but among these, extrusion using a circular die or a T-die is preferred. The extruded sheet is then at least in the uniaxial direction stretched in a stretching ratio of 2 to 7 times at the softening temperature or lower of the polyolefin resin according to a known process. Among the above range of the stretching ratio, 4 to 6 times are preferred. If the stretching ratio is less than 2 times, it is difficult to obtain a good water vapor permeability, while if it exceeds 7 times, stretching breakage occurs to make stabilized production impossible.

The present invention will be described in more detail by way of Examples. Physical properties of the film were evaluated according to the following methods:

Specific surface area (m²/g): measured according to BET adsorption method.

Average particle size (μm): measured by means of an instrument for measuring the powder surface area (manufactured by Shimadzu S isakusyo), by filling its sample (3g) in a sample cylinder of 2 cm² X 1 cm and measuring the time of air permeation (5cm³) under 50 mm water pressure.

Tensile strength at break (kg): according to JIS P-8113 using samples of 25 mm wide X 100 mm long; grip separation rate 200 mm/min., the tensile strength at break was measured MD (machine direction) and in TD (transverse direction to MD), respectively.

Water vapor permeability: measured according to ASTM-E-96-66.

Softness: Evaluation was made by hand touch as follows:

A: very soft

B: somewhat soft

5 C: considerably hard

Examples 1 to 9

Inorganic fine powders [precipitated barium sulfate (Examples 1 to 4 and 8 to 9), precipitated calcium carbonate (Examples 5 and 6) or magnesium oxide (Example 7)] having a specific surface area and an average particle size indicated in Table 1 were added to a linear low density polyethylene of MI=2 (L-LDPE (Examples 1 to 7)), a low density polyethylene of MI=5 (LDPE (Example 8)) or a polypropylene of MI=1.5 (PP (Example 9)) in quantities indicated in Table 1, followed by blending the mixture by means of a Henschel mixer (tradename), pelletizing the blend, making the pellets into a film by extrusion, and then uniaxially roll-stretching the film to 2 to 7 times the original length at 50 °C to obtain a porous film of 20 µm thick. The physical properties of the film were then measured. The results are shown in Table 1.

Example 10

20 A film made from the same composition as in Example 2 was stretched to (3 X 3) times in the longitudinal direction simultaneously with the traverse direction at 70 °C by means of a biaxially stretching machine to obtain a porous film of 20 µm thick. The evaluation results of its physical properties are shown in Table 1.

Example 11

25 Twenty % by weight of a linear low density polyethylene (L-LDPE) of MI=2, 20% by weight of a low density polyethylene (LDPE) of MI=5 and 60% by weight of precipitated barium sulfate having a specific surface area of 4.1 m²/g and an average particle size of 0.8 µm were blended to obtain a porous film in the same manner as in Example 1. The evaluation results of its physical properties are shown in Table 1.

Comparative Examples 1 to 6

Porous films were prepared in the same manner as in Example 1 except that inorganic fine powders [precipitated barium sulfate (Comparative Examples 1 to 3 and 5 to 6) or calcium carbonate (Comparative Example 4)] under varied kinds, filled quantities and stretching conditions as indicated in Table 1 were blended with a L-LDPE in varied quantities. The evaluation results of their physical properties are shown in Table 1. In Comparative Example 1, since the quantity of fine powders added is less than 30%, the porosity lowers and the water vapor permeability is small. In Comparative Example 2, since the quantity of fine powders added exceeds 80%, the stretchability lowers and stretching breakage occurs in a stretching ratio of 1.5 times. In Comparative Examples 3 and 4, since the specific surface area of the fine powders exceeds 15 m²/g, the stretchability lowered and foaming was observed at the time of extrusion by means of a sheet molding machine, and split. In Comparative Example 5, since the average particle size of fine powders exceeds 4 µm, the stretchability lowered so that it is impossible to effect a stabilized production in a stretching ratio of twice. In Comparative Example 6, since the stretching ratio is less than twice, no sufficient water vapor permeability can be obtained.

Since the film of the present invention is sufficiently porous, the water vapor permeability and air permeability are good and also the water resistance is superior. Particularly since its flexibility is good to afford a soft hand, it is suitable for clothings, particularly for sanitary use application. As compared with prior art, it is possible to produce even an extremely thin film of 20 µm thick or less; thus the resulting porous film scarcely has use application where it is used as a single product, but its main use application is directed to its lamination onto non-woven fabric, pulp, nylon taffeta. The thinner the film, the less the cost, and further, a specific feature is exhibited that at the time of clothing, the fitting feeling due to the thickness of the lamination is not uncomfortable.

55

Table 1

	Basic resin		Inorganic fine powders			Stretch ratio (times)	Tensile strength at break (kg)		Water vapor permeability (g/m ² 24 hrs)	Flexibility
	Kind	Amount added (wt%)	Kind	Specific surface area (m ² /g)	Average particle size (μm)		MD	TD		
Example 1	L-LDPE	30	Precipitated BaSO ₄	4.1	0.8	70	2	3.0	1.0	A
2	"	40	"	"	"	60	5	4.0	0.5	A
3	"	65	"	"	"	35	7	5.5	0.3	A
4	"	50	"	8.0	0.5	50	6	5.0	0.4	A
5	"	40	Precipitated CaCO ₃	14.0	0.5	60	4	5.8	0.4	B
6	"	60	"	5.5	3.0	40	5	4.2	0.5	B
7	"	50	MgO	7	1.1	50	5	4.3	0.4	B
8	LDPE	40	Precipitated BaSO ₄	4.1	0.8	60	4	3.0	0.3	B
9	PP	30	"	4.1	0.8	70	6	6.0	0.3	B
10	L-LDPE	40	"	4.1	0.8	60	3 x 3	4.5	3.8	A
11	L-LDPE	40	"	4.1	0.8	60	6	4.5	0.3	A
Comparative ex. 1	L-LDPE	80	Precipitated BaSO ₄	4.1	0.8	20	8	6.5	0.1	C
2	"	10	"	4.1	0.8	90				
3	"	50	"	18.3	0.3	50				
4	"	70	CaCO ₃	16.5	1.0	30				
5	"	60	Precipitated BaSO ₄	0.8	4.5	40	2	2.8	0.8	B
6	"	40	Precipitated BaSO ₄	4.1	0.8	60	1.5	2.5	1.5	C

55 Claims

1. A process for producing a porous film comprising melting a composition consisting essentially of a polyolefin resin and a filler non-compatible therewith, forming the molten composition into a film and

then stretching the film to 2 to 7 times the original length at least in the uniaxial direction, characterized in that 30 to 80 parts by weight of an inorganic fine powder having a spherical shape, a specific surface area of 15 m²/g or less and an average particle size of 0.4 to 4 µm are blended with 20 to 70 parts by weight of the polyolefin resin, these parts by weight being based on 100 parts by weight of the blend.

2. A process according to claim 1 wherein the fine powder is selected from calcium carbonate, magnesium carbonate, magnesium oxide, barium sulfate, silica, aluminum hydroxide and alumina.

3. A process according to claim 1 or 2 wherein the fine powder is precipitated calcium carbonate or precipitated barium sulfate.

4. A process according to any one of claims 1 to 3 wherein the polyolefin resin is a linear low density polyethylene resin or a blend containing it.

Revendications

1. Procédé de production d'un film poreux comprenant la fusion d'une composition consistant essentiellement en une résine polyoléfinique et une charge non compatible avec celle-ci, la transformation de la composition fondue en un film, puis l'étirage du film à 2 à 7 fois sa longueur originale au moins dans le sens uniaxial, caractérisé en ce que 30 à 80 parties en poids d'une poudre fine minérale ayant une forme sphérique, une surface effective inférieure ou égale à 15 m²/g et une granulométrie moyenne comprise entre 0,4 et 4 µm sont mélangées à 20 à 70 parties en poids de la résine polyoléfinique, ces parties en poids représentant 100 parties en poids de mélange.

2. Procédé selon la revendication 1, dans lequel la poudre fine est sélectionnée parmi le carbonate de calcium, le carbonate de magnésium, l'oxyde de magnésium, le sulfate de baryum, la silice, l'hydroxyde d'aluminium et l'alumine.

3. Procédé selon la revendication 1 ou 2, dans lequel la poudre fine est du carbonate de calcium précipité ou du sulfate de baryum précipité.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la résine polyoléfinique est une résine de polyéthylène basse densité linéaire ou un mélange contenant ce dernier.

Patentansprüche

1. Verfahren zur Herstellung einer porösen Folie, umfassend das Schmelzen einer Zusammensetzung, die im wesentlichen aus einem Polyolefinharz und einem mit diesem nicht kompatiblen Füllmaterial besteht, das Verformen der geschmolzenen Zusammensetzung zu einer Folie und danach das Verstrecken der Folie auf das zwei- bis siebenfache der ursprünglichen Länge wenigstens in monoaxialer Richtung, dadurch gekennzeichnet, daß 30 bis 80 Gewichtsteile eines anorganischen, feinen Pulvers mit einer kugelartigen Form, einer spezifischen Oberfläche von 15 m²/g oder weniger und einer durchschnittlichen Partikelgröße von 0,4 bis 4 µm mit 20 bis 70 Gewichtsteilen des Polyolefinharzes gemischt werden, wobei diese Gewichtsteile auf 100 Gewichtsteile der Mischung bezogen sind.

2. Verfahren nach Anspruch 1, in dem das feine Pulver ausgewählt ist unter Calciumcarbonat, Magnesiumcarbonat, Magnesiumoxid, Bariumsulfat, Siliciumdioxid, Aluminiumhydroxid und Aluminiumoxid.

3. Verfahren nach Anspruch 1 oder 2, in dem das feine Pulver ausgefälltes Calciumcarbonat oder ausgefälltes Bariumsulfat ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, in dem das Polyolefinharz ein lineares Polyolefinharz niedriger Dichte oder eine dieses enthaltende Mischung ist.